

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 10/00, 4/64	A1	(11) International Publication Number: WO 93/14132 (43) International Publication Date: 22 July 1993 (22.07.93)
(21) International Application Number: PCT/US92/10360 (22) International Filing Date: 1 December 1992 (01.12.92) (30) Priority data: 07/817,202 6 January 1992 (06.01.92) US (60) Parent Application or Grant (63) Related by Continuation US 07/817,202 (CIP) Filed on 6 January 1992 (06.01.92) (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).	(72) Inventors; and (75) Inventors/Applicants (for US only) : KOLTHAMMER, Brian, W., S. [US/US]; 54 Royal Oak Circle, Lake Jackson, TX 77566 (US). CARDWELL, Robert, S. [US/US]; 106 Any Way, Lake Jackson, TX 77566 (US). TRACY, John, C. [US/US]; 107 Old Angleton Road, Lake Jackson, TX 77566 (US). (74) Agent: DELINE, Douglas, N.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: CA, FI, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims and statement.</i>	
(54) Title: IMPROVED CATALYST COMPOSITION (57) Abstract An addition polymerization catalyst comprising a cationic complex of a Group 4 metal cyclopentadienyl derivative and an alumoxane shows improved resistance to catalyst poisons.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CC	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TC	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

IMPROVED CATALYST COMPOSITION

Cross-Reference to Related Application

This is a continuation-in-part of U.S. Serial No. 07/817,202, filed January 6, 1992,
5 the teachings of which are herein incorporated by reference.

Background of the Invention

This invention relates to compositions of matter which are useful as addition
polymerization catalysts, to a method for preparing these catalysts and to a method of using
these catalysts. More particularly, this invention relates to catalyst compositions useful as
10 olefin polymerization catalysts and to a method for polymerizing olefin monomers using the
same.

In EP-A 416,815, published March 13, 1991, there are disclosed certain constrained
geometry complexes comprising a constrain inducing delocalized π -bonded moiety and metals
of Groups 4-10 of the Periodic Table of the Elements. Such compositions formed catalysts in the
15 presence of activating cocatalysts such as alkylalumoxanes, aluminum alkyls, aluminum halides,
aluminum alkylhalides, Lewis acids, ammonium salts, noninterfering oxidizing agents and
mixtures of the foregoing.

In US-A 5,026,798 and US-A 5,055,438 Group IVB metallocene compounds having
a heteroatom ligand in combination with an alumoxane were disclosed as suitable olefin
20 polymerization catalysts.

In EP-A 418,044, published March 20, 1991 (equivalent to U.S. Serial No.
07/758,654) and in U.S. Serial No. 07/758,660 certain cationic derivatives of the foregoing
constrained geometry catalysts that are highly useful as olefin polymerization catalysts are
disclosed and claimed. In U.S. Serial Number 720,041, filed June 24, 1991, certain borane
25 derivatives of the foregoing constrained geometry catalysts are disclosed and a method for
their preparation taught and claimed.

For the teachings contained therein, the aforementioned pending United States
Patent applications, issued United States Patents and published European Patent Applicati ns
are herein incorporated in their entirety by reference thereto.

Although previously known cationic catalysts, especially the cationic catalysts disclosed in the foregoing applications and publications, have excellent activity, they are extremely sensitive to catalyst poisons, such as polar impurities, that may be contained in a polymerization mixture. Because of this fact, catalyst lifetimes have been limited and
 5 molecular weights of the resulting polymers have been reduced.

It is previously known in the art to utilize adjuvants such as trialkylboron and trialkylaluminum compounds to remove catalyst poisons from biscyclopentadienyl containing olefin polymerization catalysts. Disadvantageously however, such adjuvants have proven to be ineffective in combating the inhibition of cationic catalysts, especially cationic, constrained
 10 geometry catalysts, and when used in the polymerization of olefin monomers especially, actually may interfere with the desired catalytic process.

In J. Am. Chem. Soc., 113, 8570-8571 (1991), it has furthermore been reported that the use of alumoxanes in combination with biscyclopentadienyl containing cationic catalysts results in detrimental interference with the catalyst for propylene polymerizations.

15 It would be desirable if there were provided improved, cationic catalyst compositions having constrained geometry that are resistant to the effects of catalyst poisons.

In particular, it would be desirable if there were provided improved, cationic, constrained geometry, catalyst compositions having extended catalyst lifetimes and improved polymerization efficiencies.

20 Summary of the Invention

The present investigations have led to certain improved cationic catalyst compositions that are highly active as addition polymerization catalysts and desirably have improved resistance to catalyst poisons.

According to the present invention there is now provided a catalyst composition
 25 comprising in combination:
 a cationic complex of the formula: $\text{CpMYX}_n + \text{A}^-$,
 wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to Cp;

30 n is zero or one, depending on the oxidation state of M;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R'' , said divalent moiety, R'' , having from 1 to 50 atoms and being covalently bonded to Y, Cp further may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl
 35 groups containing up to 20 non-hydrogen atoms;

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C_{1-20} hydrocarbyl, and Y together with R'' , Cp and M forms a metallocycle;

X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and

A⁻ is an inert, noncoordinating anion, and

5 an alumoxane;

the molar ratio of alumoxane to cationic complex being from 0.1:1 to 50:1.

The foregoing catalyst compositions in a preferred embodiment comprise the reaction product of:

a) an organometallic complex of the formula:

10 CpMYX_nR ,

wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to Cp;

n is zero or one, depending on the oxidation state of M;

15 R is hydride or C₁₋₂₀ hydrocarbyl;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R", said divalent moiety, R", having from 1 to 50 atoms and being covalently bonded to Y, Cp further may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl

20 groups containing up to 20 non-hydrogen atoms; and

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C₁₋₂₀ hydrocarbyl, and Y together with R", Cp and M forms a metallocycle; and X, if any, is a monovalent substituent selected from:

25 hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, phosphine groups, and mixtures thereof, said groups having up to 20 non-hydrogen atoms;

b) an active compound or complex, B', capable of converting the organometallic complex a) into a cationic complex of the formula: $\text{CpMYX}_n + \text{A}'$,

where Cp, M, Y, X and n are as previously defined, and A' is the anion resulting from the combination of B' and R which is abstracted from complex a) or A' is the counterion from complex B'; and

30 c) an alumoxane;

the molar ratio of components b):a) being from 0.1:1 to 50:1, and the molar ratio of components c):a) being from 1:1 to 10,000:1.

The above compositions are usefully employed in the polymerization of addition 35 polymerizable monomers, especially C₂₋₂₀ α -olefins, including mixtures thereof, to prepare polymers for molding, film, sheet, extrusion foaming and other applications.

Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic
 5 Table of the Elements using the IUPAC system for numbering groups.

The compositions of the present invention may be thought of as forming a mixture of a cationic species having a charge limited structure corresponding to the formula: $\text{CpMYX}_n + \text{A}^-$, and the alumoxane, c).

Suitable alumoxanes preferably include C_{1-4} alkylalumoxanes, especially
 10 methylalumoxane. Both cyclic and linear alumoxanes as well as mixtures thereof are suitable. Alumoxanes are well known in the art and methods for their preparation are illustrated by US-A 4,542,199, 4,544,762, 5,015,749, and 5,041,585. Particularly preferred alumoxanes are so called modified alumoxanes, that are completely soluble in alkane solvents, especially heptane, and include very little, if any, trialkylaluminum contaminant. A technique for preparing such a
 15 modified alumoxane has been disclosed in US-A 5,041,584. The teachings of the foregoing United States patents are incorporated herein in their entireties by reference thereto.

Active compounds, B', useful as component b) are those compounds capable of abstraction of the R substituent from a) to form an inert, noninterfering counter ion. A preferred active compound is tris(perfluorophenyl)boron. This compound results in the
 20 formation of an anionic species, A'^- , that is $\text{RB}(\text{C}_6\text{F}_5)_3^-$, where R is hydride or C_{1-20} hydrocarbyl.

Examples of complexes useful as component b) include salts of a Bronsted acid and a noncoordinating, compatible anion. More particularly the non-coordinating, compatible anion may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as
 25 used herein, includes non-metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

As used herein, the recitation "noncoordinating, compatible anion" means an anion which either does not coordinate to component a) or which is only weakly coordinated therewith remaining sufficiently labile to be displaced by a neutral Lewis base. A non-
 30 coordinating, compatible anion specifically refers to a compatible anion which when functioning as a charge balancing anion in the catalyst system of this invention, does not transfer an anionic substituent or fragment thereof to said cation thereby forming a neutral four coordinate metallocene and a neutral metal byproduct. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are
 35 noninterfering with desired subsequent polymerizations.

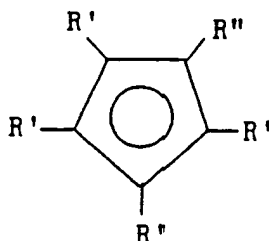
Preferred complexes useful as component b) are ferrocenium salts or silver salts of tetrakis(perfluorophenyl)borate. These components result in the formation of the anionic species, $\text{B}(\text{C}_6\text{F}_5)_4^-$, which is A^- .

It should be noted that alkylaluminum oxanes are not satisfactory for use as component b).

Component a) is preferably a cyclopentadienyl group containing complex of a Group 4 metal. The preferred X group, if any, is an alkyl, aryl, silyl, germyl, aryloxy, or alkoxy group having up to 20 non-hydrogen atoms. It should be noted that additional neutral Lewis base compounds may also be associated with the metal complex by coordinate covalent or other weaker bonding forces. Such compounds include ethers, phosphines, amines, etc. However, the presence of such neutral coordinating ligands is not preferred.

More preferably, Cp is depicted by the formula:

10



15

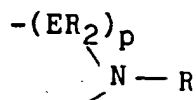
wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, alkyl and silyl groups of up to 4 non-hydrogen atoms; and

R'' is -BR- or -ER₂- wherein E is a member of Group 14 of the Periodic Table of the Elements, and R is as previously defined.

20

In a highly preferred embodiment R''-Y- is



wherein:

E independently each occurrence is carbon, silicon, or germanium;

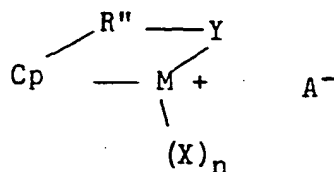
p is an integer from 1 to 4; and

R is as previously defined.

30

Preferred cationic complexes formed by contacting components a) and b) correspond to the formula:

35



wherein:

Cp, R'', Y, X, M, n and A⁻ are as previously defined.

Most preferably:

M is zirconium or titanium;

Cp is a cyclopentadienyl group substituted with R'' or such a cyclopentadienyl group further substituted with up to four C₁₋₄ alkyl groups;

R'' is C₁₋₄ dialkylsilanediyl especially dimethylsilanediyl;

Y is C₁₋₄ alkylamido;

X is C₁₋₄ alkyl, benzyl or 2-dimethylaminobenzyl;

n is one; and

A⁻ is RB(C₆F₅)₃⁻ or B(C₆F₅)₄⁻, where R is as previously defined.

The preferred ratio of components b):a) is 0.95:1 to 10:1, more preferably 1:1 to 5:1. The preferred ratio of component c):a) is 2:1 to 100:1, most preferably 3:1 to 10:1.

In general, the catalyst composition can be prepared by combining the components in a suitable solvent or diluent at a temperature within the range from -100 to 300°C, preferably 25 to 75°C. Suitable solvents or diluents include any of the compounds known in the prior art to be useful as solvents or diluents in the polymerization of olefins, diolefins and acetylenically unsaturated monomers. Suitable compounds include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and mixtures thereof and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and mixtures thereof. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, and mixtures thereof. Mixtures of two or more of the foregoing solvents may also be used if desired.

The catalyst compositions are used in addition polymerizations using conditions well known in the prior art. It will, of course, be appreciated that the catalyst composition will form *in situ* if the components thereof are added directly to the polymerization process. However, it is preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization reactor. The respective components may be combined

in any order of addition to form the catalyst composition of the invention. The catalysts and components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium.

In a preferred embodiment, the catalyst is used to polymerize C_{2-20} α -olefins and mixtures thereof, particularly ethylene or propylene, most preferably ethylene, at a temperature within the range from 0°C to 220°C, preferably 25°C to 160°C and at a pressure within the range from atmospheric to 6,900 kPa (1000 psig) preferably 100 kPa to 4,800 kPa (15 to 700 psig). In a most preferred embodiment of the present invention, the catalyst is used either to homopolymerize ethylene or to copolymerize ethylene with a lower α -olefin having from 3 to 8 carbon atoms (including styrene) thereby yielding a copolymer. In both the preferred and most preferred embodiments, the monomers will be maintained at polymerization conditions for a time from 1 to 60 minutes. Suitably the catalyst will be used at a concentration from 10^{-7} to 10^{-1} moles per mole of monomer. A solvent for the reactants and/or the polymer may be used if desired.

Having thus broadly described the present invention it is believed that the same will become even more apparent by reference to the following examples. It will be appreciated, however, that the examples are presented solely for the purpose of illustration and should not be construed as limiting the invention.

Examples 1-3

20 Catalyst Preparation

A known weight of the organometallic complex, (t-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dimethyl ($Me_4C_5-Me_2Si-N-t-Bu$)Ti(CH₃)₂, was dissolved in toluene to give a clear, 0.005M solution. The complex was prepared from ($Me_4C_5-Me_2Si-N-t-Bu$)TiCl₂ as disclosed in U.S. Serial No. 758,654, filed September 12, 1991 (equivalent to EP-A 418,044 published March 20, 1991). The dichloride salt in turn was prepared according to the method outlined in U.S. Serial No. 545,403, filed July 3, 1990, (equivalent to EP-A 416,815). A cationic complex solution of 10 mL total volume was prepared by adding 6.0 mL of mixed alkane solvent (Isopar™ E, available from Exxon Chemical Inc.), 2.0 mL of the Ti reagent solution and 2.0 mL of a 0.010 M solution of tris(perfluorophenyl)boron in toluene to a 250 ml glass bottle. The solution was mixed for a few minutes and transferred by syringe to a catalyst injection cylinder on the polymerization reactor.

Polymerizations

A stirred, one-gallon (3.79L) autoclave reactor was charge with two liters of Isopar™ E containing varying amounts of methylalumoxane (MAO) solution and 150 mL of octene-1 which had been partially purified by passing over a molecular sieve bed before heating to reaction temperature. The reactor was charged with ethylene sufficient to bring the total pressure to 450 psig (3.1 MPa). An amount of the cationic complex solution as described

under catalyst preparation was injected into the reactor. The reactor temperature and pressure were maintained constant at the desired final pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. The rate and duration of the reaction were monitored by measuring the demand flow of ethylene to the reactor for each polymerization. Ethylene/1-octene copolymer yield (reported as g PE) was calculated based on mass flow of ethylene to the reactor during the run. Results as a function of MAO content are contained in Table 1.

Table 1

<u>Example</u>	<u>Ti (μMole)</u>	<u>B:Ti^a</u>	<u>Al^b (μMole)</u>	<u>Al:Ti</u>	<u>Yield (gPE)</u>
A*	10	2:1	0	0	46
B*	10	2:1	0	0	32
1	10	2:1	50	5	70
2	10	2:1	100	10	222
3	10	2:1	200	20	222

* Comparative, not an example of the invention, no MAO.

a Molar ratio boron:titanium

b Aluminum value represented by methylalumoxane.

It may be seen that improved polymer yields result under these reaction conditions from the use of the catalyst composition of the present invention.

Example 4

The polymerization of Examples 1-3 was repeated excepting that the 1-octene employed is not purified prior to use in the reactor. Results are contained in Table 2.

Table 2

<u>Example</u>	<u>Ti (μMole)</u>	<u>B:Ti^a</u>	<u>Al^b (μMole)</u>	<u>Al:Ti</u>	<u>Yield (gPE)</u>
C*	10	2:1	0	0	0
4	10	2:1	130	13	211

* Comparative, not an example of the invention, no MAO.

a molar ratio boron:titanium

b aluminum value represented by methylalumoxane.

The improvement in resistance to catalyst poisons is clearly illustrated by comparison of the results in Table 2.

Examples 5-6

The reaction conditions of Examples 1-3 were repeated excepting that the catalyst composition was prepared separately by combining all three components before injecting the same into the reactor. Comparative tests omitting the boron component, and substituting triethylaluminum for methylalumoxane are also performed. Results are contained in Table 3.

Table 3

<u>Example</u>	<u>Ti</u> <u>(μMole)</u>	<u>B:Ti^a</u>	<u>Al^b</u> <u>μ(Mole)</u>	<u>Al:Ti</u>	<u>Yield</u> <u>(gPE)</u>
5 ^c	7.5	2:1	75	10	247
6 ^d	7.5	2:1	75	10	214
D ^{*e}	7.5	0	375	50	0
E ^{*f}	7.5	2:1	75	10	10

*Comparative, not an example of the invention.

a Molar ratio boron:titanium.

b Aluminum value represented by methylalumoxane.

c The titanium complex was mixed with tetrakis(perfluorophenyl)boron then added to MAO solution in Isopar™ E.

d A MAO solution in Isopar™ E was mixed with tetrakis(perfluorophenyl)boron and the titanium complex added last.

e Boron component omitted.

f Triethylaluminum substituted for MAO.

By examination of the results of Table 3 it may be seen that formation of a cationic species is necessary and that trialkylaluminum is not substantially effective in place of MAO.

Examples 7-17

The reaction conditions of Examples 1-3 were repeated using different titanium complexes, temperatures, octene contents, hydrogen pressures and alumoxanes. In Example 7, the titanium complex was (t-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dibenzyl, prepared by a method analogous to that of Example 1. In Example 8 the titanium complex was (t-butylamido)dimethyl(tetrahydrofluorenyl)silanetitanium dimethyl, also prepared by a method analogous to that of Example 1. All reactions were conducted at 120°C excepting Examples 13 and 14 that were conducted at 140°C and 160°C respectively. Moles of octene were 1.0 excepting for run 11,

when 0.5 moles were used. In Examples 15-17 and the comparative examples, the 1-octene feed was highly purified by first contacting with a molecular sieve bed followed by contacting with an alumina based deoxygenating agent (Q-5, available from Engelhard Corporation). All polymers were recovered, devolatilized and dried to determine yield. Polymer properties were tested by standard techniques. Results are contained in Table 4.

10

15

20

25

30

35

Table 4

Example	Hydrogen (mmole)	Ti (μMole)	B (μMole)	Al (μMole)	Yield (gPE)	Efficiency (gPE/μMole Ti)	Density	I ₂ ^a	I ₁₀ /I ₂ ^b
7 ^c	10	7.5	15	75	152	20,300	0.9098	2.23	5.74
8 ^c	10	7.5	15	75	96	12,800	0.8972	2.02	6.56
9 ^c	0	7.5	15	75	193	25,700	0.8998	0.13	8.85
10 ^c	20	7.5	15	75	227	30,300	0.9109	13.50	6.17
11 ^c	10	7.5	15	75	210	28,000	0.9233	3.37	6.00
12 ^d	0	4	8	40	245	61,300	0.9033	0.80	8.70
13 ^d	0	6	12	60	215	35,800	0.9060	0.74	8.02
14 ^d	0	8	16	80	140	17,500	0.9118	1.96	7.09
15 ^d	0	3	6	30	135	45,000	0.9011	0.16	6.86
F ^d	0	7.5	15	0	162	21,600	0.9070	0.45	7.52
16 ^d	4	3	6	30	160	53,000	0.9039	1.09	6.25
G ^d	4	7.5	15	0	170	22,700	0.9085	2.56	6.42
17 ^d	30	3	6	30	155	51,700	0.9128	52.60	5.51
H ^d	30	7.5	15	0	161	21,500	0.9175	125.00	5.93

*Comparative, not an example of the invention.

a I₂ is measured according to ASTM D-1238 and indicates melt flow properties. Higher values of I₂ indicate greater melt flow.

b I₁₀ is measured according to ASTM D-1238.

c Methylalumoxane having molecular weight 1200 available from Schering A.G. in toluene.

d Methylaluminoxane was modified methylalumoxane, prepared according to USP 5,041,584, available from Texas Alkyls.

By reference to Table 4 it may be seen that hydrogen may be utilized to control polymer melt flow properties and in the presence of alumoxane the effect of hydrogen can be moderated. Thus the catalyst is not extremely sensitive to the presence of hydrogen.

5

10

15

20

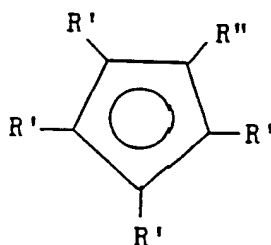
25

30

35

WHAT IS CLAIMED IS:

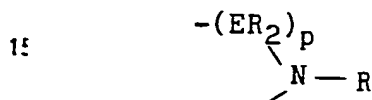
1. A catalyst composition comprising in combination:
a cationic complex of the formula: $\text{CpM}^+\text{YX}_n + \text{A}^-$,
5 wherein:
M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of 3 or 4, bound in an η^5 bonding mode to Cp;
n is zero or one, depending on the oxidation state of M;
Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or
10 octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R^* , said divalent moiety, R^* , having from 1 to 50 atoms and being covalently bonded to Y, Cp further may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms;
Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -
15 S-, wherein R is C_{1-20} hydrocarbyl, and Y together with R^* , Cp and M forms a metallocycle;
X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and
A⁻ is an inert, noncoordinating anion, and
20 an alumoxane;
the molar ratio of alumoxane to cationic complex being from 0.1:1 to 50:1.
2. A catalyst composition according to claim 1 wherein A⁻ is $\text{RB}(\text{C}_6\text{F}_5)_3^-$ or $\text{B}(\text{C}_6\text{F}_5)_4^-$, where R is hydride or C_{1-20} hydrocarbyl.
- 25 3. The catalyst composition according to claim 1 wherein Cp is depicted by the formula:



wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, alkyl and silyl groups of up to 4 non-hydrogen atoms; and
 10 R'' is -BR- or -ER₂- wherein E is a member of Group 14 of the Periodic Table of the Elements, and R is C₁₋₂₀ hydrocarbyl.

4. The catalyst composition according to claim 3 wherein R''-Y- is

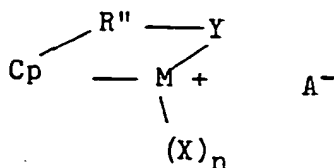


wherein:

E independently each occurrence is carbon, silicon, or germanium;
 20 p is an integer from 1 to 4; and
 R is C₁₋₂₀ hydrocarbyl.

5. The catalyst composition according to claim 1 wherein the cationic complex corresponds to the formula:

25



30

wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of 3 or 4, bound in an η^5 bonding mode to Cp;

n is zero or one, depending on the oxidation state of M;

35 Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R'', said divalent moiety, R'', having from 1 to 50 atoms and being covalently bonded to Y, Cp further

may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms;

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C₁₋₂₀ hydrocarbyl, and Y together with Rⁿ, Cp and M forms a metallocycle;

5 X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and

A⁻ is an inert, noncoordinating anion.

6. A catalyst composition comprising the reaction product of:

10 a) an organometallic complex of the formula:



wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to Cp;

15 n is zero or one, depending on the oxidation state of M;

R is hydride or C₁₋₂₀ hydrocarbyl;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Rⁿ, said divalent moiety, Rⁿ, having from 1 to 50 atoms and being covalently bonded to Y, Cp further
20 may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms; and

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C₁₋₂₀ hydrocarbyl, and Y together with Rⁿ, Cp and M forms a metallocycle; and

25 X, if any, is a monovalent substituent selected from: hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, phosphine groups, and mixtures thereof, said groups having up to 20 non-hydrogen atoms;

b) an active compound or complex, B', capable of converting the organometallic complex a) into a cationic complex of the formula: $\text{CpMYX}_n^+ \text{A}^-$,

30 where Cp, M, Y, X and n are as previously defined, and A⁻ is the anion resulting from the combination of B' and R which is abstracted from complex a) or A⁻ is the counterion from complex B'; and

c) an alumoxane;

the molar ratio of components b):a) being from 0.1:1 to 50:1, and the molar ratio of components c):a) being from 1:1 to 10,000:1.

35 7. A process for polymerizing an olefin, diolefin or acetylenic compound comprising contacting the olefin, diolefin or acetylenic compound or mixture thereof with a composition according to Claims 1 to 6 under polymerization conditions and recovering the resulting polymer.

AMENDED CLAIMS

[received by the International Bureau on 12 March 1993 (12.03.93);
new claims 8 and 9 added; other claims unchanged (2 pages)]

may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms;

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C₁₋₂₀ hydrocarbyl, and Y together with Rⁿ, Cp and M forms a metallocycle;

5 X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and

A⁻ is an inert, noncoordinating anion.

6. A catalyst composition comprising the reaction product of:

10 a) an organometallic complex of the formula:



wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to Cp;

15 n is zero or one, depending on the oxidation state of M;

R is hydride or C₁₋₂₀ hydrocarbyl;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Rⁿ, said divalent moiety, Rⁿ, having from 1 to 50 atoms and being covalently bonded to Y, Cp further
20 may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms; and

Y is a divalent substituent selected from groups of the formula -NR-, -PR-, -O- or -S-, wherein R is C₁₋₂₀ hydrocarbyl, and Y together with Rⁿ, Cp and M forms a metallocycle; and

X, if any, is a monovalent substituent selected from:

25 hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, phosphine groups, and mixtures thereof, said groups having up to 20 non-hydrogen atoms;

b) an active compound or complex, B', capable of converting the organometallic complex a) into a cationic complex of the formula: CpMYX_nA^+ ,

30 where Cp, M, Y, X and n are as previously defined, and A⁺ is the anion resulting from the combination of B' and R which is abstracted from complex a) or A⁺ is the counterion from complex B'; and

c) an alumoxane;

the molar ratio of components b):a) being from 0.1:1 to 50:1, and the molar ratio of components c):a) being from 1:1 to 10,000:1.

35 7. A process for polymerizing an olefin, diolefin or acetylenic compound comprising contacting the olefin, diolefin or acetylenic compound or mixture thereof with a composition according to Claims 1 or 6 under polymerization conditions and recovering the resulting polymer.

8. A cationic complex of the formula: $\text{CpMYX}_n + \text{A}^-$,

wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of 3 bound in an η^5 bonding mode to Cp;

5 n is zero;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R'' , said divalent moiety, R'' , having from 1 to 50 atoms and being covalently bonded to Y, Cp further may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms;

Y is a divalent substituent selected from groups of the formula $-\text{NR}-$, $-\text{PR}-$, $-\text{O}-$ or $-\text{S}-$, wherein R is C_{1-20} hydrocarbyl, and Y together with R'' , Cp and M forms a metallocycle;

X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and
15 A^- is an inert, noncoordinating anion.

9. A cationic complex corresponding to the formula:



wherein:

M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of 3 bound in an η^5 bonding mode to Cp;

n is zero;

Cp is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, R'' , said divalent moiety, R'' , having from 1 to 50 atoms and being covalently bonded to Y, Cp further may be substituted with from 1 to 4 alkyl, halogen, aryl, haloalkyl, alkoxy, aryloxy or silyl groups containing up to 20 non-hydrogen atoms;

Y is a divalent substituent selected from groups of the formula $-\text{NR}-$, $-\text{PR}-$, $-\text{O}-$ or $-\text{S}-$, wherein R is C_{1-20} hydrocarbyl, and Y together with R'' , Cp and M forms a metallocycle;

X, if any, is a monovalent substituent selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and phosphine groups, and combinations thereof, said groups or combination having up to 20 non-hydrogen atoms; and
35 A^- is an inert, noncoordinating anion.

STATEMENT UNDER ARTICLE 19

New claims 8 and 9 have been added to claim the cationic complexes disclosed wherein n is equal to zero and M is a Group 4 metal in an oxidation state of $+3$. Such novel complexes are disclosed in the present application as having utility in combination with an alumoxane as addition polymerization catalysts. Such disclosure is found in the application at page 2, line 26 to page 3, line 4, and page 5, line 31 to page 6, line 17.

INTERNATIONAL SEARCH REPORT

PCT/US 92/10360

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F10/00; C08F4/64		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 418 044 (THE DOW CHEMICAL COMPANY) 20 March 1991 cited in the application see the whole document ---	1-7
P,Y	EP,A,0 513 380 (IDEMITSU KOSAN COMPANY) 19 November 1992 see claims 1-3,9; examples 18,32 see page 9, line 18 - line 54 ---	1-7
P,Y	WO,A,9 200 333 (EXXON CHEMICALS PATENTS INC.) 9 January 1992 see claims 1-26; examples 1-4 ---	1-7
P,Y	EP,A,0 481 480 (IDEMITSU KOSAN COMPANY) 22 April 1992 see claims 1,2 see page 4, line 54 - line 55 ---	1-7
	-/--	
¹⁰ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
10 FEBRUARY 1993	25.02.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FISCHER B.R.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 426 638 (FINA TECHNOLOGY, INC) 8 May 1991 see claim 25 -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210360
SA 67689

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10/02/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0418044	20-03-91	US-A- 5064802	12-11-91
		AU-A- 6247390	21-03-91
		CA-A- 2025332	15-03-91
		CN-A- 1050194	27-03-91
		JP-A- 3139504	13-06-91
		US-A- 5132380	21-07-92
EP-A-0513380	19-11-92	WO-A- 9209640	11-06-92
WO-A-9200333	09-01-92	None	
EP-A-0481480	22-04-92	US-A- 5171919	15-12-92
EP-A-0426638	08-05-91	CA-A- 2027122	01-05-91
		CN-A- 1051365	15-05-91
		JP-A- 3207704	11-09-91

